Reliability in Chemical Footprint Modelling of Consumer Products

MÉLANIE DOUZIECH

PhD Thesis Radboud University (4.12.2019)
Promotoren: Prof. dr. M.A.J. Huijbregts and Prof. dr. H. King
Co-Promotoren: Dr. R. van Zelm and Dr. R. Oldenkamp

Product Environmental Footprint

Chemical footprint

Ecotoxicity

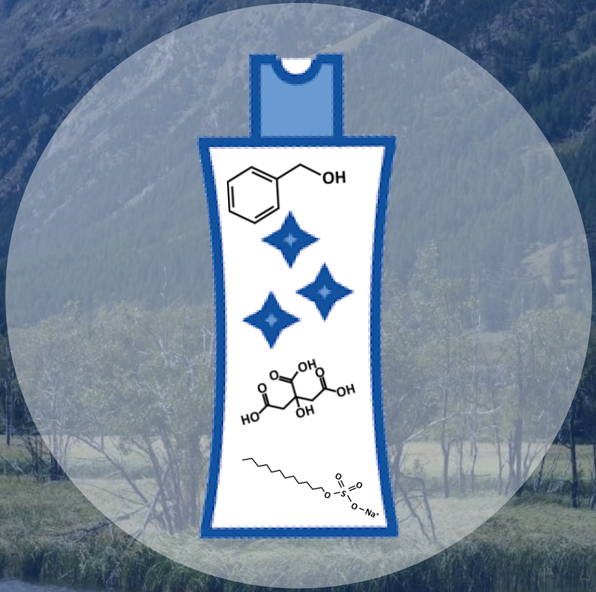
Chemicals

Land

Raw material sourcing

Climate

Energy use



Biodiversity

Raw material sourcing

Water

Availability

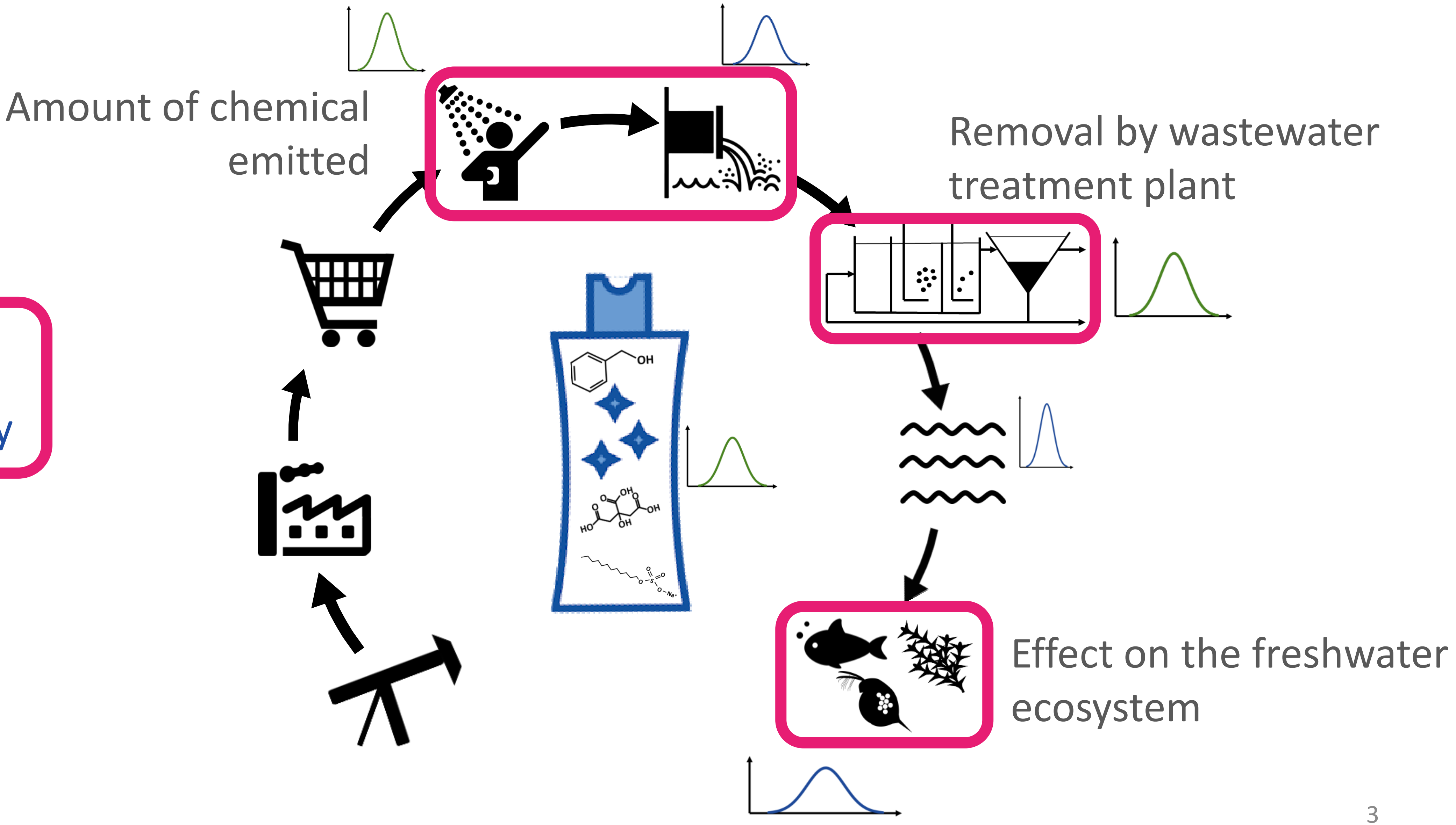
Human toxicity

Chemicals

Reliability in chemical footprint modelling

Variability

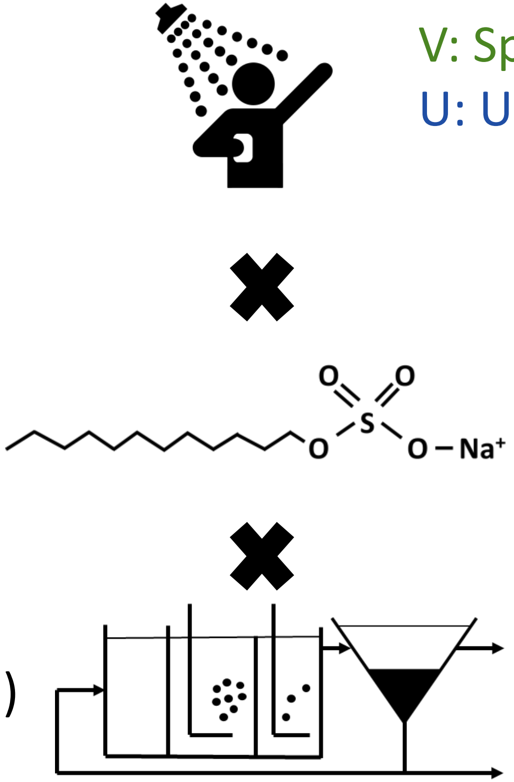
Uncertainty



Amount of chemical emitted

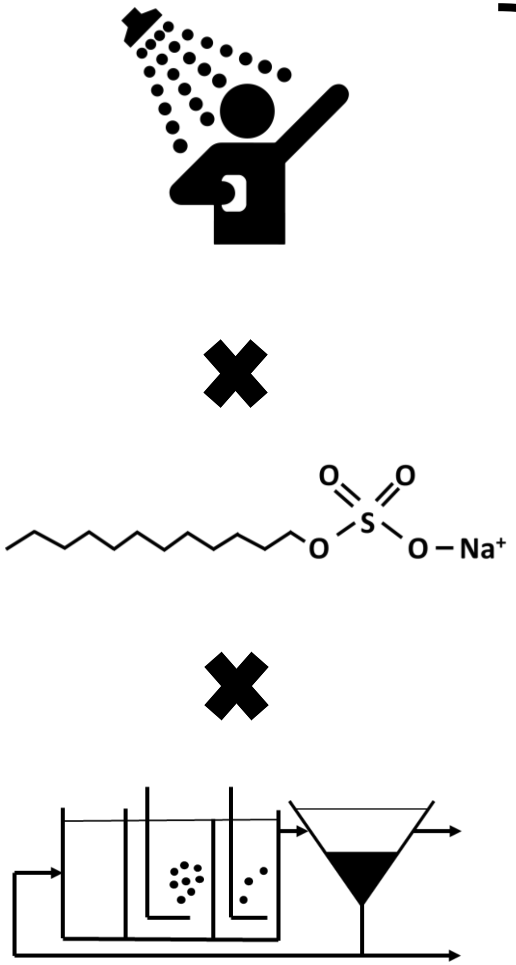
- **Chemicals** emitted yearly from **personal care products use** and their **range**
  - Consumer surveys from France, the Netherlands, South Korea, and the USA
  - Three products: shampoo, conditioner, bodywash
  - Three surfactants and two preservatives

1. Product used individually
   - Use habit survey data for average individual use (**U**)
   - Four different countries (**V**)
2. Chemical fraction in product
   - Patent data, published formulations (**U**)
3. Fraction removed
   - Estimated with SimpleTreat from the chemical properties (**U**)
   - Number of connected persons (**V**)

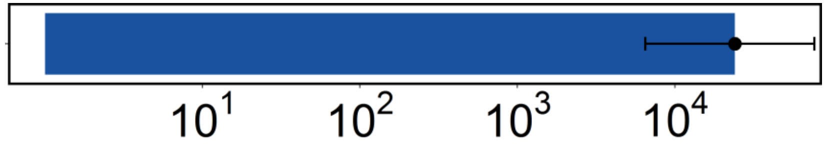


V: Spatial Variability
U: Uncertainty

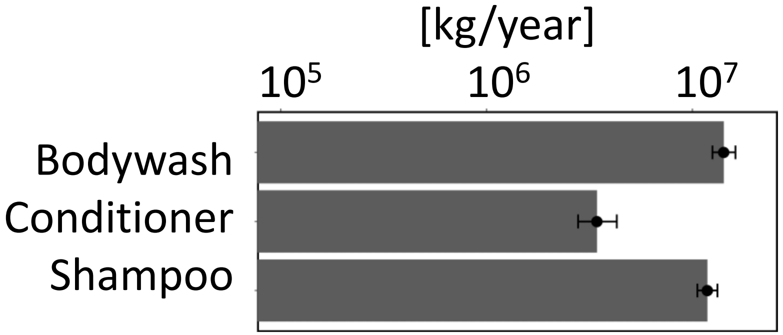
Amount of chemical emitted

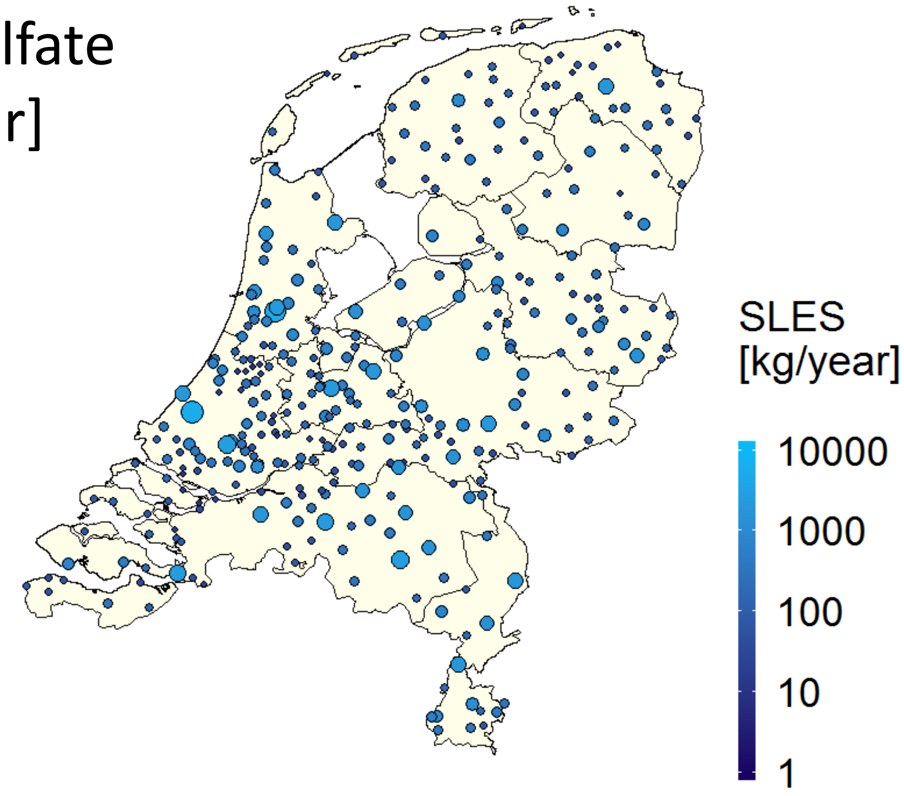


Release of sodium lauryl ether sulfate (SLES) in the Netherlands [kg/year]



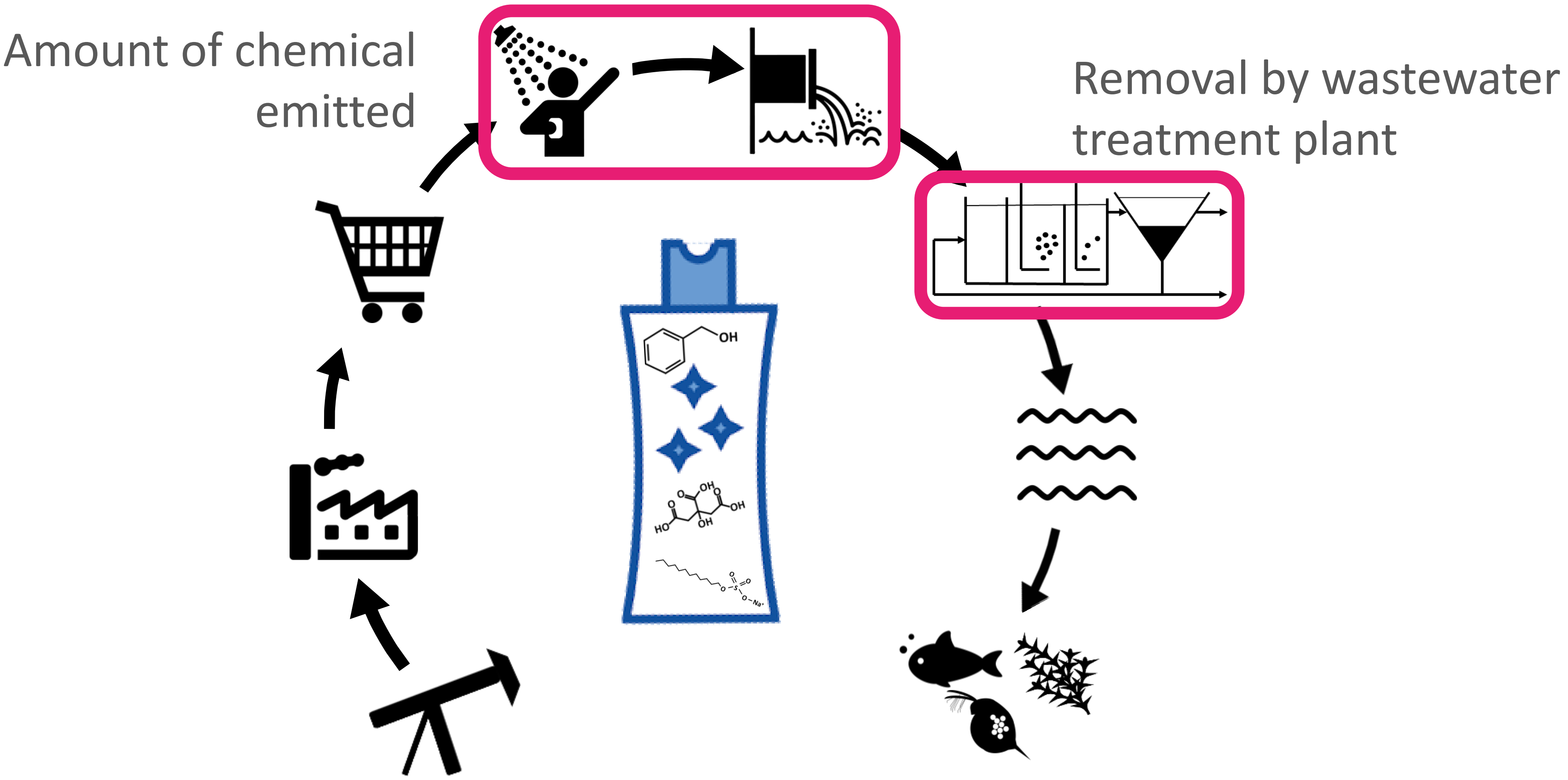
from the use of





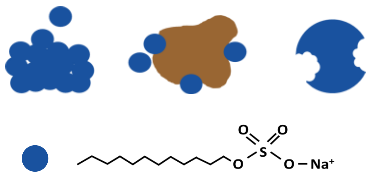
- Uncertainty from fraction removed
- Spatial variability important for hotspots identification
- Drawbacks: data requirement, variability in study design

Reliability in chemical footprint modelling

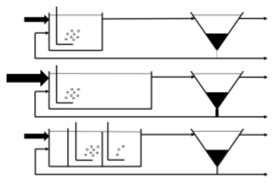


Removal by wastewater treatment plants

- Quantify the **influence** of **internal** and **external** factors on the **removal efficiencies** of a set of chemicals in activated sludge WWTPs



Internal
Physico-chemical properties



External
Technological variability

1539 measured removal efficiencies of fragrances, surfactants, and pharmaceuticals + physico-chemical properties

Meta-analysis: Effect size $= \ln\left(\frac{\bar{X}_{C_{eff}}}{\bar{X}_{C_{in}}}\right)$

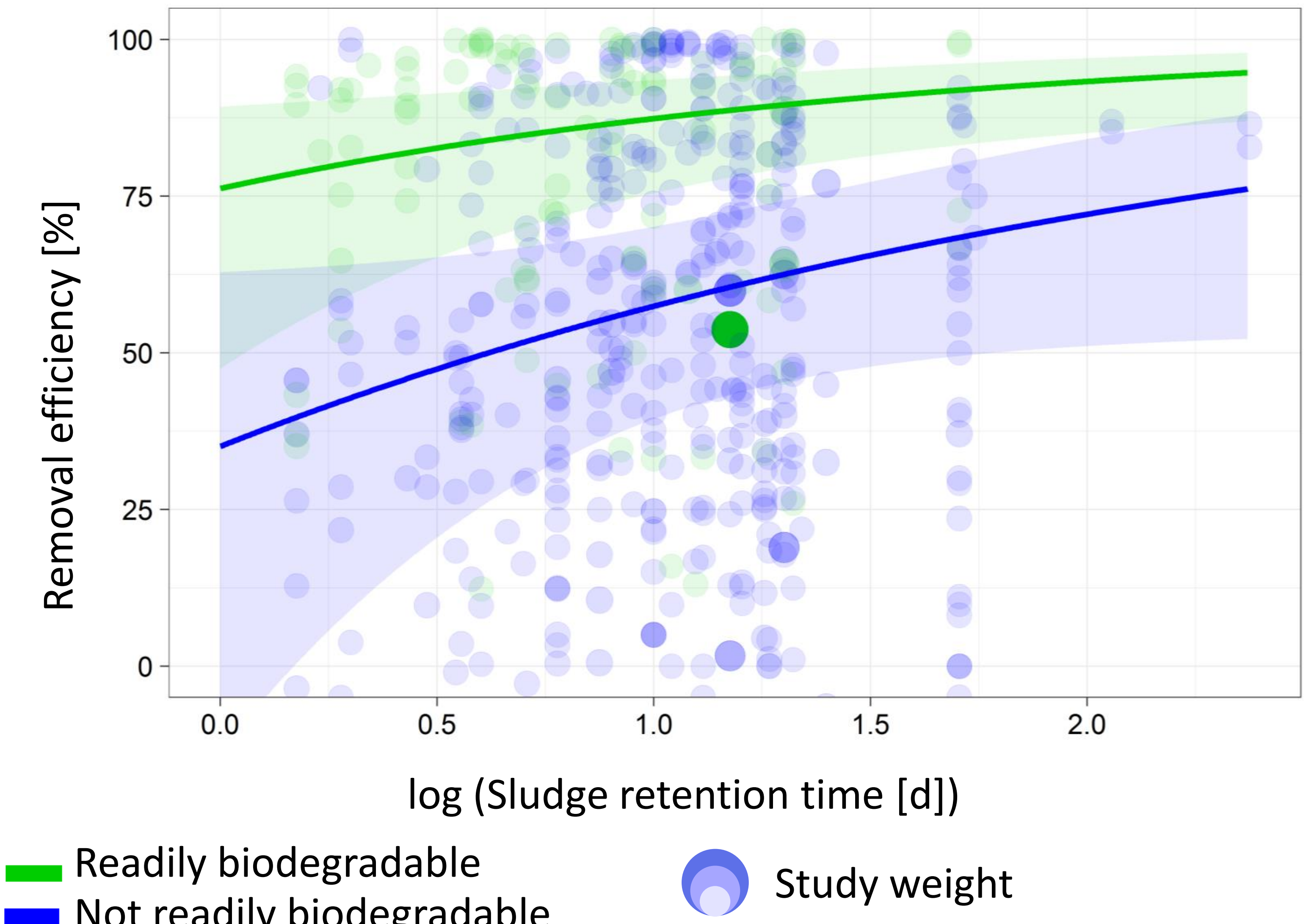
Mixed-effects model (542 data points)

$$\ln\left(\frac{\bar{X}_{C_{eff}}}{\bar{X}_{C_{in}}}\right) = \underbrace{\beta_0 + \beta_1 x_1 + \cdots + \beta_p x_p}_{\text{Fixed effects}} + \underbrace{u_i}_{\text{Random effects}}$$

Fixed effects
Internal and external factors

Random effects
Study, chemical, country, WWTP

Removal by wastewater treatment plants

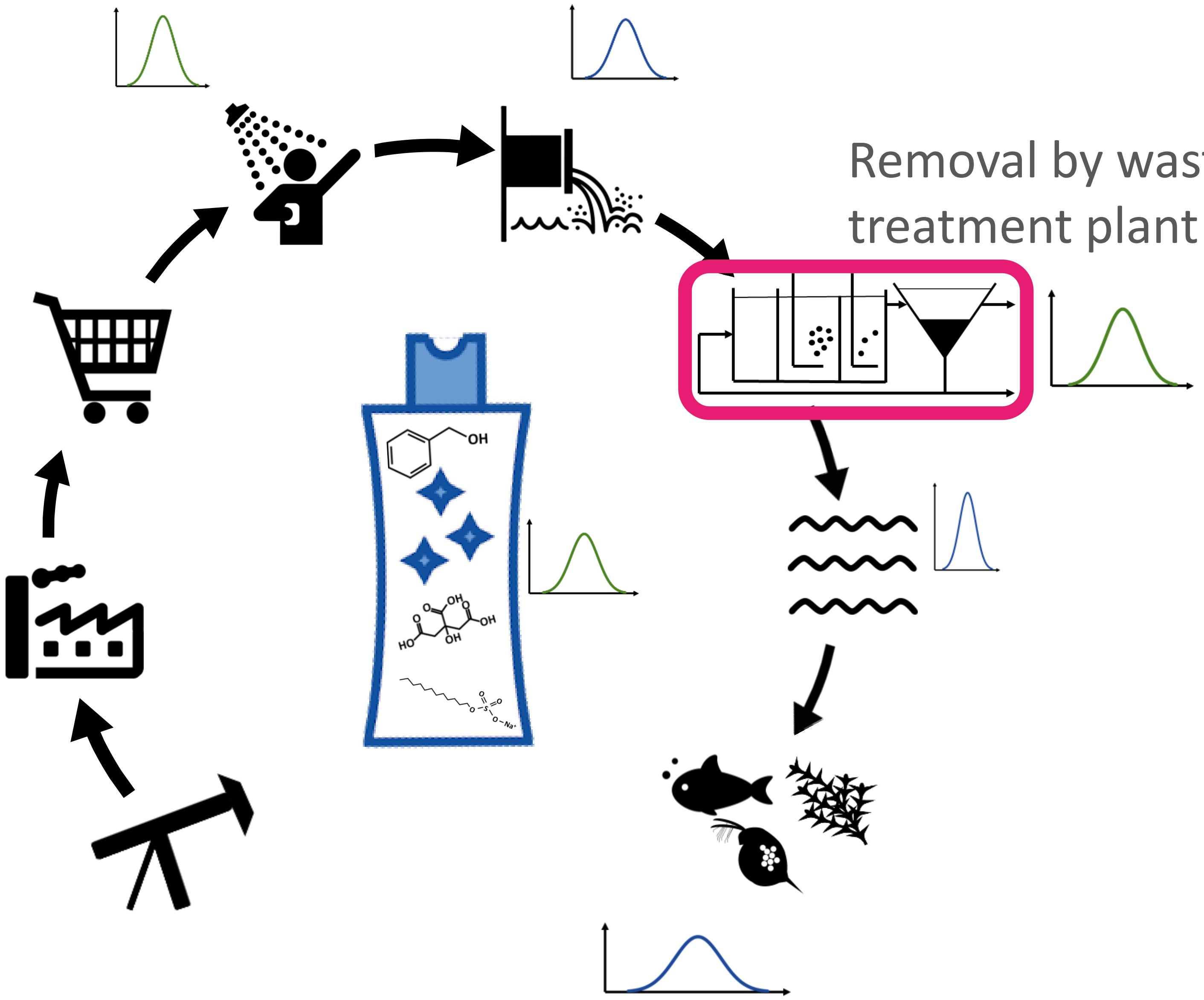


- High mean weighted removal efficiency (82%)
- Readily biodegradable better removed than not readily biodegradable ones
- Improve predictive performance
  - Deconjugation processes
  - Electrochemical interactions

Reliability in chemical footprint modelling

Variability

Uncertainty

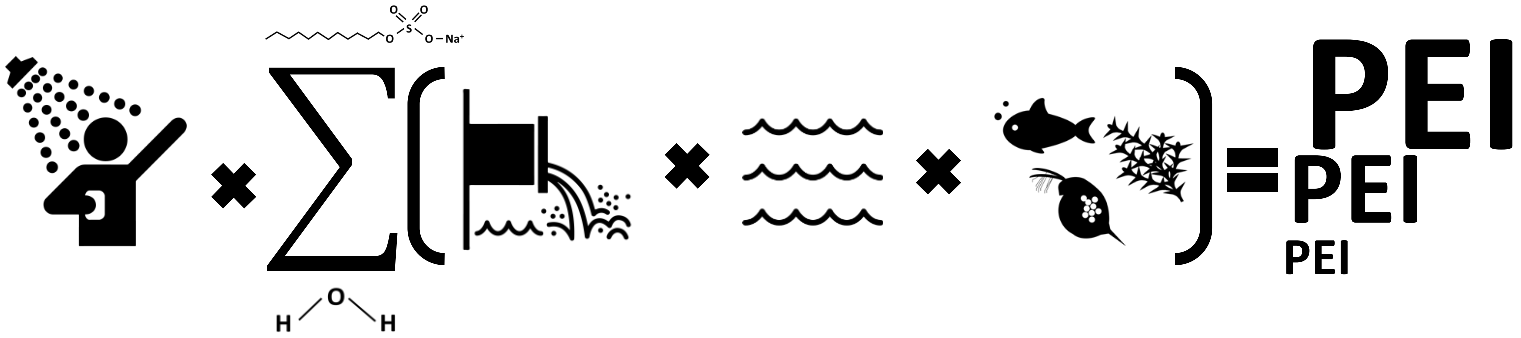


Removal by wastewater treatment plant

Sources of variability and uncertainty

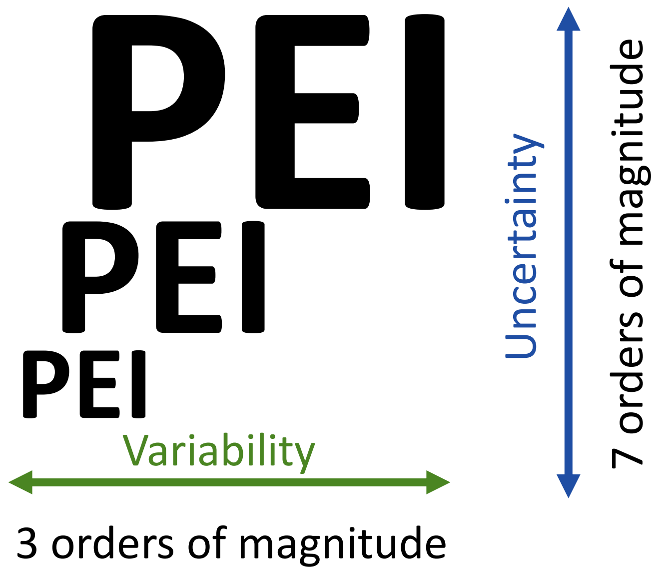
- Influence of **variable** and **uncertain** parameters on the **Potential ecotoxicological impact** (PEI) of a shampoo use

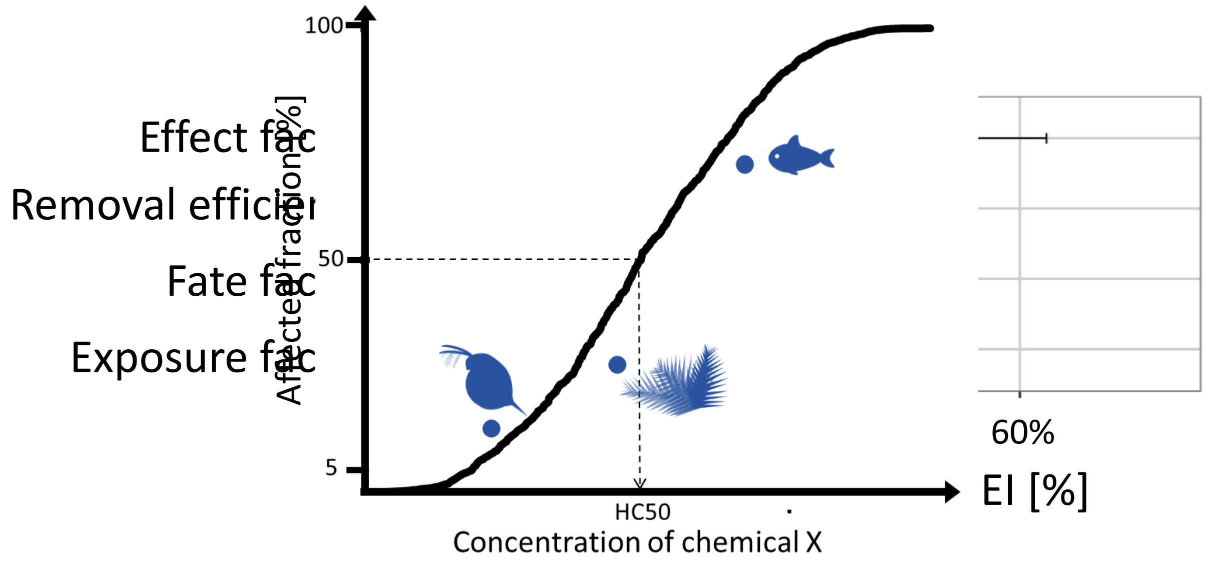
→ 2D Monte Carlo Simulation



Shampoo used A_P	Fraction of chemical entering the environment $F_{mass,c,P}$ and E_C	Fate of chemical $FF_{c,r}$ and $XF_{c,r}$	Potential effect on aquatic species EF_c

Sources of variability and uncertainty



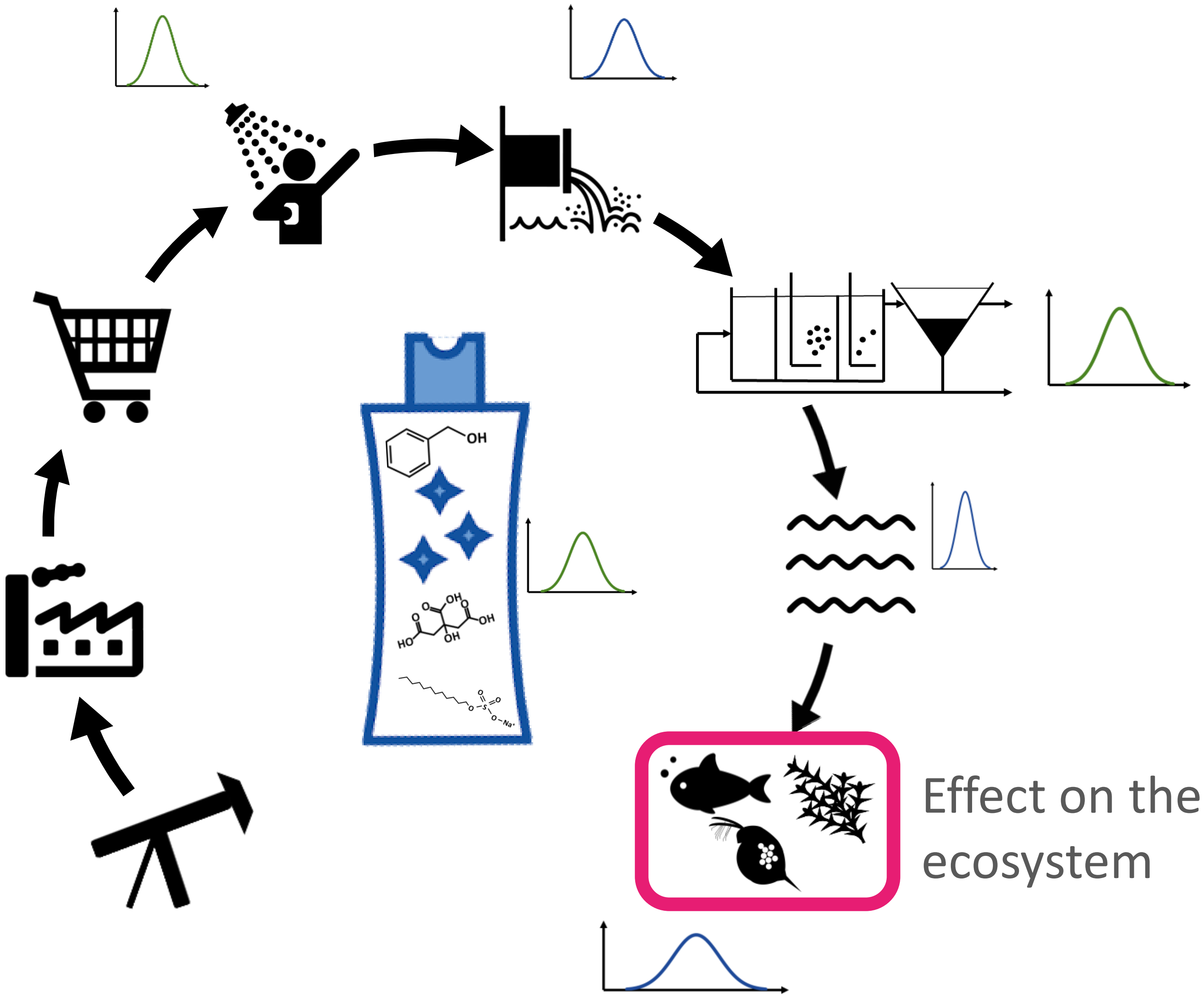


- Variability in shampoo composition important
- Spread driven by the uncertainty in the potential effect on aquatic ecosystems
- Effect factor (=0.5/HC50) based on ecotoxicity values from only three species

Reliability in chemical footprint modelling

Variability

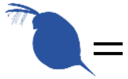
Uncertainty



Effect on the freshwater ecosystem

Effect on the freshwater ecosystem

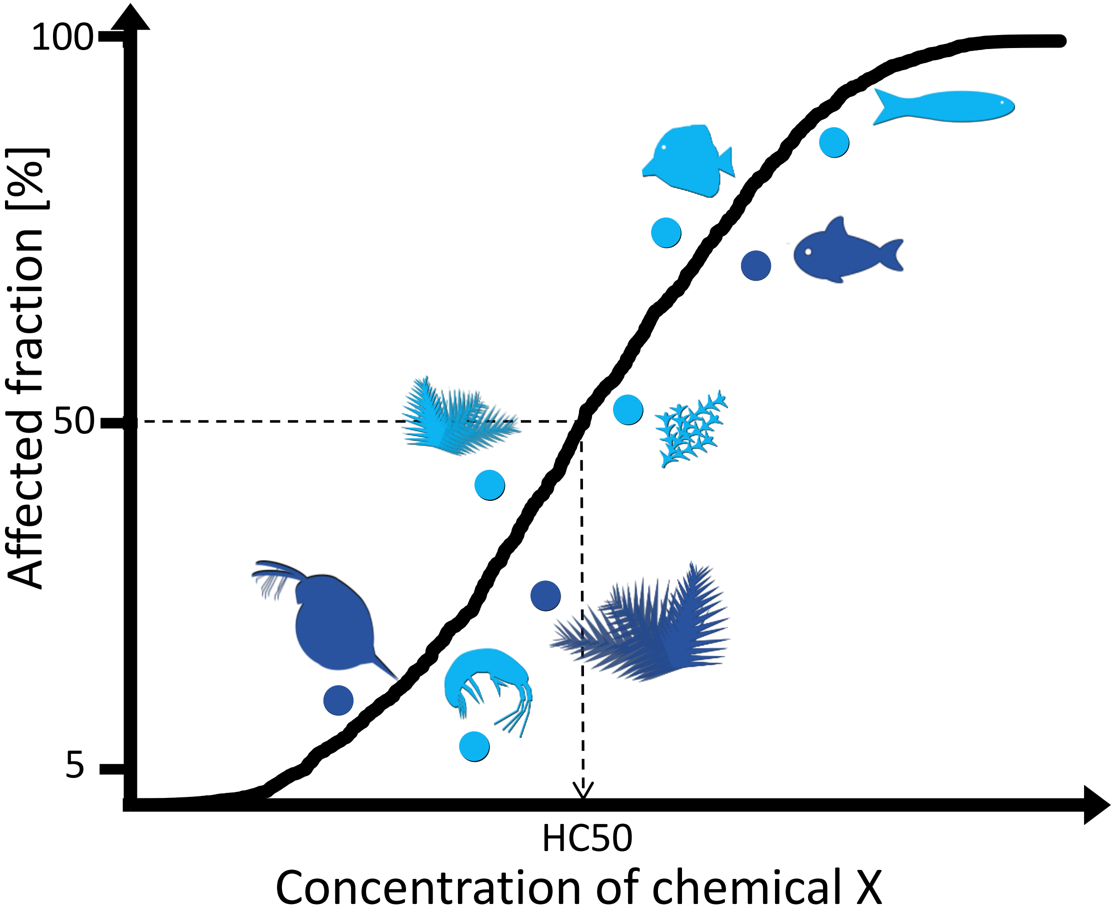
- **Reliable** and **representative hazardous concentrations** estimated from ***in silico*** methods
    1. Quantitative Structure Activity Relationships (QSARs)

        $= f(Chemical\ properties)$

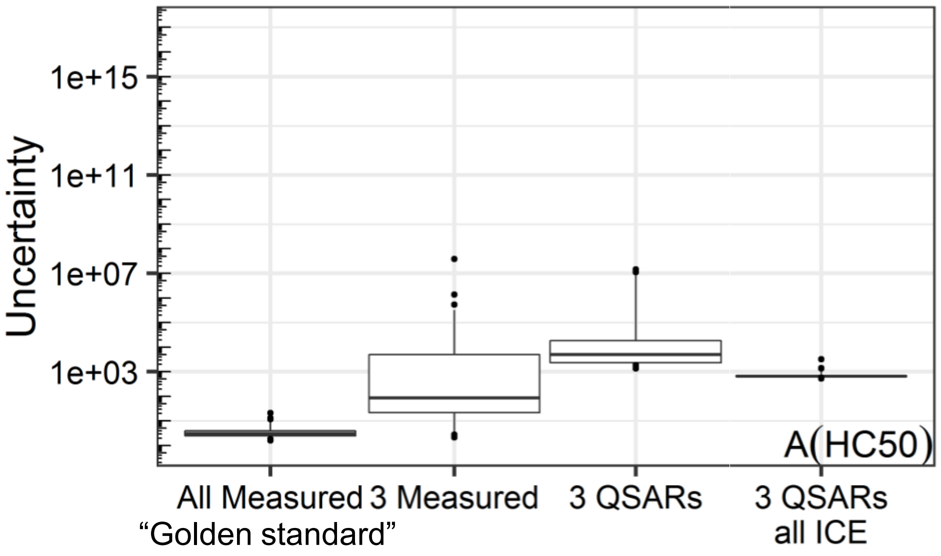
    2. Interspecies Correlation Estimation (ICE) equations

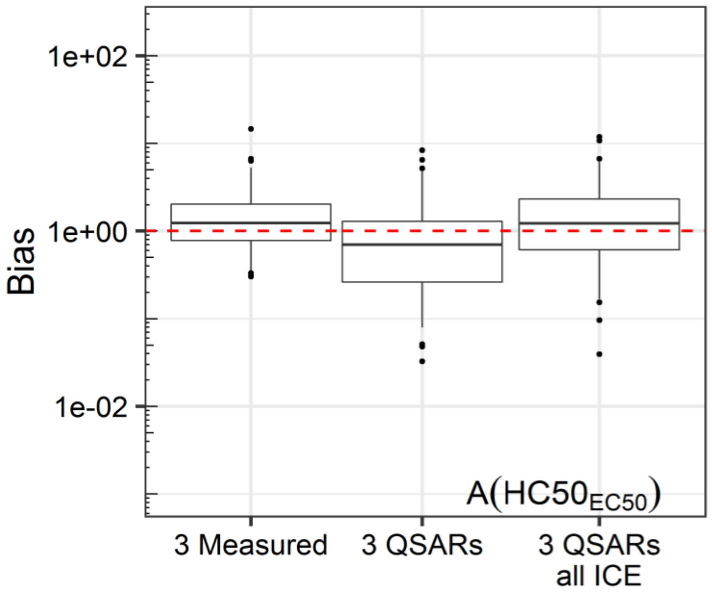
        $= a + b \cdot$ 

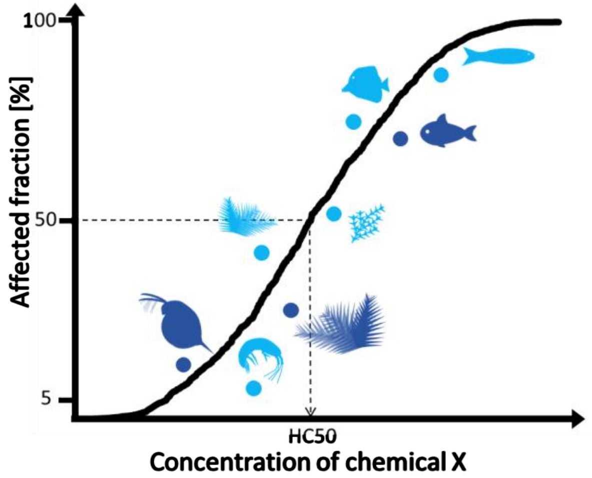
- Reliable: Uncertainty in QSAR and ICE, sampling uncertainty
- Representative: Bias = $HCx_{AllMeasured}$ / $HCx_{estimated}$



Effect on the freshwater ecosystem



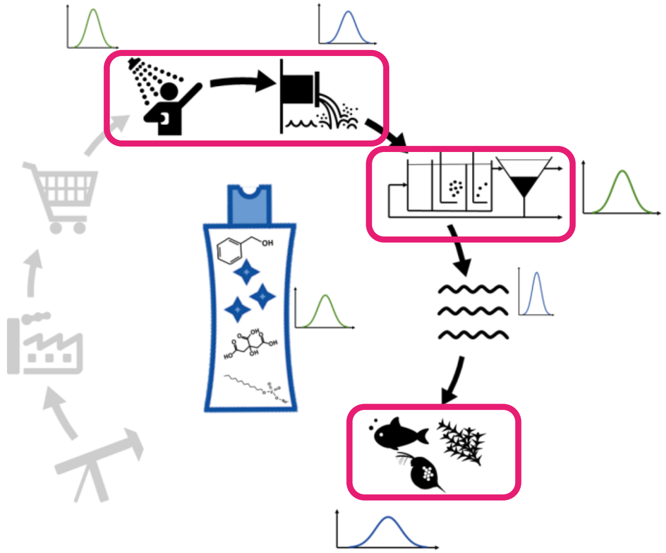




Median	3.1	99.4	$4.5 \cdot 10^3$	$6.1 \cdot 10^2$	Median	1.24	0.7	1.22

- Combining QSAR and ICE leads to hazardous concentrations
  - With lower spread in uncertainty compared to 3 measured
  - With comparable bias to 3 measured
- Chemicals with few ecotoxicity data (Applicability domain !)

Reliability in chemical footprint modelling



- Important to include product formulation
- Know the size of wastewater treatment plants to identify hotspots
- Improve modelled removal efficiencies from wastewater treatment plants
  - Deconjugation processes
  - Electrochemical interactions
- Reduce uncertainty of the chemical effect quantification using *in silico* approaches
- 5 articles with 19 citations maximum (total 34)

melanie.douziech@mines-paristech.fr

ADDITIONAL SLIDES

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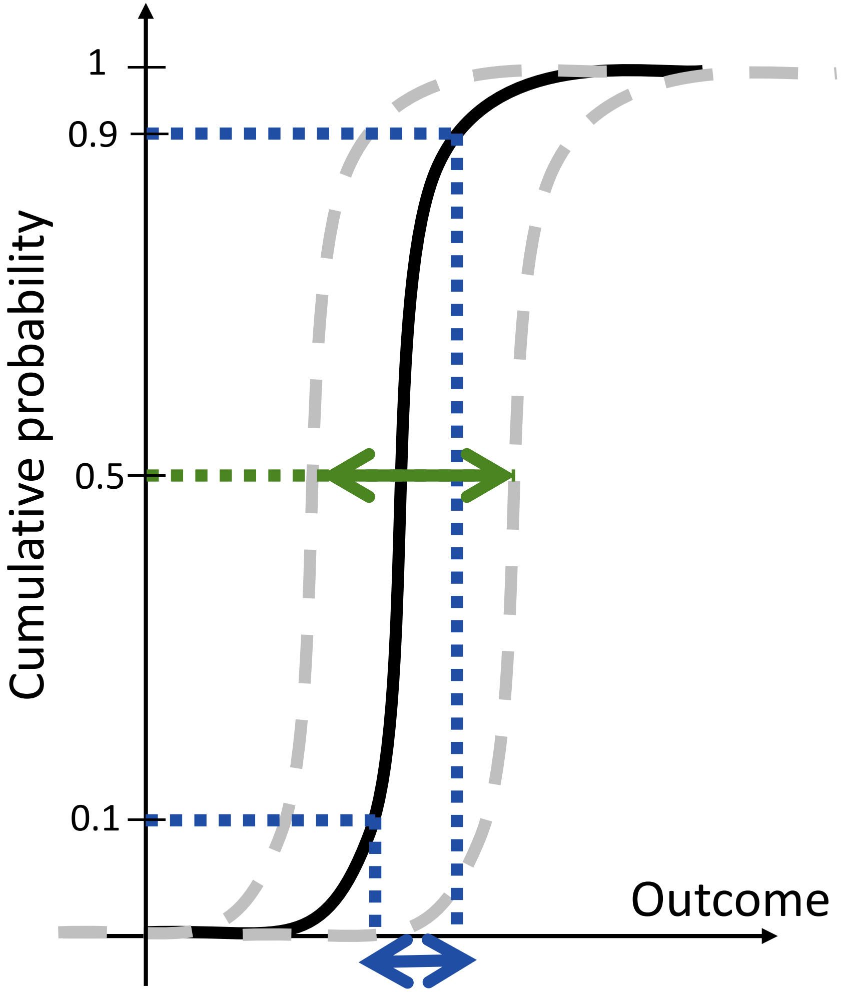
2D Monte Carlo Simulation



Uncertainty ratio or Variability ratio = $\dfrac{p90}{p10}$

Sources of uncertainty and variability

Parameter	Uncertainty	Variability
A_P	n.a.	Inter-individual variability in product use habits
$F_{mass,c,P}$	n.a.	Each product formulation considered was used as the starting point to compute a set of PEI while varying the uncertain and variable parameters
$FF_{c.r}$	Vapor pressure at 25°C (P_{vap}), solubility at 25°C (Sol), organic carbon-water partitioning coefficient (K_{OC}), pKa (negative base-10 logarithm of the acid dissociation constant), and degradation rate constants in air (k_{degA}), water (k_{degW}), sediment (k_{degSd}), and soil (k_{degSl})	Spatial variability from the 16 regions implemented in USEtox
XF_c	pKa and organic carbon-water partitioning coefficient (K_{OC})	Spatial variability from the 16 regions implemented in USEtox
E_c	Vapour pressure at 25°C (P_{vap}), solubility at 25°C (Sol), organic carbon-water partitioning coefficient (K_{OC}), pKa, and degradation rate constants in wastewater (k_{degWW})	Technological variability between activated sludge wastewater treatment plants (WWTPs) (Franco et al. 2013)
EF_c	Ecotoxicity values; Limited sample size	

Chapter 5 Table 6

Sources of uncertainty and variability

Quantification of uncertainty for physico-chemical properties

a. QSAR training data set available

Property	$\bar{x}$	Uncertainty quantification	n	Estimation Method
P_{vap}	Log (P_{vap})	(Mendenhall et al. 2009)	3037	(EPA 2012), MPBVP Help
Sol	Log (*Sol*)	(Mendenhall et al. 2009)	817	(EPA 2012), WSKOWWIN Help
K_{OC} acid	Log (K_{OC})	(Mendenhall et al. 2009)	62	(Franco and Trapp 2008)
K_{OC} base	Log (K_{OC})	(Mendenhall et al. 2009)	66	(ECETOC 2013)
K_{OC} neutral	Log (K_{OC})	(Mendenhall et al. 2009)	81	(Sablijc et al. 1995)
$EC50_{PeCPs}$	p*EC50*	(Mendenhall et al. 2009) and published mean squared errors.	72 D. magna 20 P. subcapitata 67 P. promelas	(Gramatica et al. 2014; Gramatica et al. 2016; Gramatica et al. 2013)

b. QSAR training data set not available – Error in estimating mean value only

Property	$\bar{x}$	Uncertainty quantification	Estimation Method
pKa	*pKa*	Standard deviation provided by estimation program per chemical	(ACD/Labs 2017) and Unilever internal documentation
k_{degA}		Standard deviation derived from the coefficient of variation of 0.4	(van Zelm and Huijbregts 2013)
$EC50_{ECOSAR}$	*EC50*	Lognormal distribution following (Reuschenbach et al. 2008)	(EPA 2017)
HC50	Log (*HC50*)	Standard deviation from estimated EC50 values	(Huijbregts et al. 2010)

c. Specific approaches

Property	$\bar{x}$	Uncertainty quantification	Estimation Programme
DT50	Log (*median(DT50)*)	Vary according to category (Appendix A.5, Section A.5.2)	(Aronson et al. 2006; Sarfraz Iqbal et al. 2013)
k_{degW}	Derived from degradation rate constant (DT50): $k_{degW} = \ln(2)/DT50$		
k_{degSd}	Derived from degradation rate constant (DT50): $k_{degSd} = \ln(2)/(DT50/9)$		
k_{degSl}	Derived from degradation rate constant (DT50): $k_{degSl} = \ln(2)/(DT50/2)$		
k_{degWW}	Derived from k_{degW}: $k_{degWW} = 30 \cdot k_{degW}$		(EPA 2017)

Chapter 5 Table 7

Sources of uncertainty and variability – Included chemicals

Chemical Name	Chemical Name	Chemical Name
2,6-dimethyl-7-octen-2-ol	dimethiconol	isopropyl myristate
4-tert-butylcyclohexyl acetate	Dipropylene Glycol constituant 1	laureth 1
5,5,6-trimethylbicyclohept-2-ylcyclohexanol	Dipropylene Glycol constituant 2	limonene
alpha-isomethyl ionone	Dipropylene Glycol constituant 3	linalool
amodimethicone	disodium EDTA	linalyl acetate
anisaldehyde	dmdm hydantoin	lysine HCL
arginine	edta	menthol
benzoic acid	ethyl hydroxypyrone	methylchloroisothiazolinone
benzophenone-4	ethyl linalool	methyldihydrojasmonate
benzyl acetate	ethyl trimethylcyclopentene butenol	methylenedioxyphenyl methylpropanal
benzyl alcohol	ethyl vanillin	methylisothiazolinone
benzyl salicylate	ethylene brassylate	methylparaben
butylphenyl methylpropional	ethylene dodecanedioate	octahydrocoumarin
c11-15 pareth-7	ethylhexyl methoxycinnamate	oxacyclohexadec-12-en-2-one, (12e)-
caffeine	gamma-decalactone	panthenol
carbomer	gamma-nonalactone	phenethyl alcohol
ceramide NG	gamma-undecalactone	phenoxyethanol
cetrimonium chloride	geraniol	phenoxyethyl isobutyrate
ci 17200	gluconolactone	phenylisohexanol
ci 19140	glucose	p-menthan-7-ol
ci 77266	glycerin	polyoxyethylene lauryl ether
cis-2-tert-butylcyclohexyl acetate	glycol distearate	propylene glycol
citric acid	grapefruit oil terpenes	salicylic acid
citronellol	guar hydroxypropyltrimonium chloride constituant 1	sodium ascorbyl phosphate
citrus aurantium dulcis (orange) peel oil	guar hydroxypropyltrimonium chloride constituant 2	sodium laureth sulfate
climbazole	hexose	tea-dodecylbenzenesulfonate
cocamide DEA constituent 1	hexyl acetate	tetramethyl acetyloctahydronaphthalenes
cocamide DEA constituent 2	hexyl cinnamal	tetrasodium EDTA
cocamide DEA constituent 3	hexyl salicylate	trehalose
cocamide MEA	hydroxypropyl methylcellulose constituant 1	trideceth-12
cocamidopropyl betaine	hydroxypropyl methylcellulose constituant 2	triethanolamine
coumarin	imidazolidinyl urea	vitamin e acetate
cyclamen aldehyde	isoamyl allylglycolate	zinc gluconate
dimethicone	Isobutenyl Methyltetrahydropyran	zinc pyrithione

Chapter 5 Table A5.4

Effect on the freshwater ecosystem – Scenarios

	Scenario	Algae	Fish	Daphnia	Other	Number of EC50
(1)	AllMeasured	All available measured EC50 values				10 to 265
(2)	3Measured	measured	measured	measured	none	3
(3)	3QSAR	QSAR	QSAR	QSAR	none	3
(4)	3QSAR-ICE	QSAR	QSAR	QSAR	all ICE estimates	100
(5)	A-F-QSAR-ICE	QSAR	QSAR	none	all ICE estimates	73
(5)	A-D-QSAR-ICE	QSAR	none	QSAR	all ICE estimates	37
(5)	F-D-QSAR-ICE	none	QSAR	QSAR	all ICE estimates	87
(6)	A-QSAR-ICE	QSAR	none	none	all ICE estimates	11
(6)	F-QSAR-ICE	none	QSAR	none	all ICE estimates	61
(6)	D-QSAR-ICE	none	none	QSAR	all ICE estimates	28

Chapter 6 Table 8

Quantifying variability in removal efficiencies of chemicals in activated sludge wastewater treatment plants–a meta-analytical approach M Douziech, IR Conesa, A Benítez-López, A Franco, M Huijbregts, ... Environmental Science: Processes & Impacts 20 (1), 171-182	19	2018
Are wave and tidal energy plants new green technologies? M Douziech, S Hellweg, F Verones Environmental science & technology 50 (14), 7870-7878	16	2016
Confronting variability with uncertainty in the ecotoxicological impact assessement of down-the-drain products MAJH Mélanie Douziech, Rik Oldenkamp, Rosalie van Zelm, Henry King, A. Jan ... Environment International 126, 37-45	10	2019
Estimation of chemical emissions from down-the-drain consumer products using consumer survey data at country and wastewater treatment plant level MAJH M Douziech, R van Zelm, R Oldenkamp, A Franco, A. J Hendriks, H King Chemosphere 193, 32-41	3	2018
Mean Species Abundance as a Measure of Ecotoxicological Risk S Hoeks, MAJ Huijbregts, M Douziech, AJ Hendriks, R Oldenkamp Environmental toxicology and chemistry 39 (11), 2304-2313	2	2020
Definition of LCA Guidelines in the Geothermal Sector to Enhance Result Comparability ML Parisi, M Douziech, L Tosti, P Pérez-López, B Mendecka, S Ulgiati, ... Energies 13 (14), 3534	2	2020
A regression-based model to predict chemical migration from packaging to food M Douziech, A Benítez-López, A Ernstoff, C Askham, AJ Hendriks, H King, ... Journal of Exposure Science & Environmental Epidemiology 30 (3), 469-477	1	2020
Reliable and representative in silico predictions of freshwater ecotoxicological hazardous concentrations M Douziech, AMJ Ragas, R van Zelm, R Oldenkamp, AJ Hendriks, H King, ... Environment international 134, 105334	1	2020